

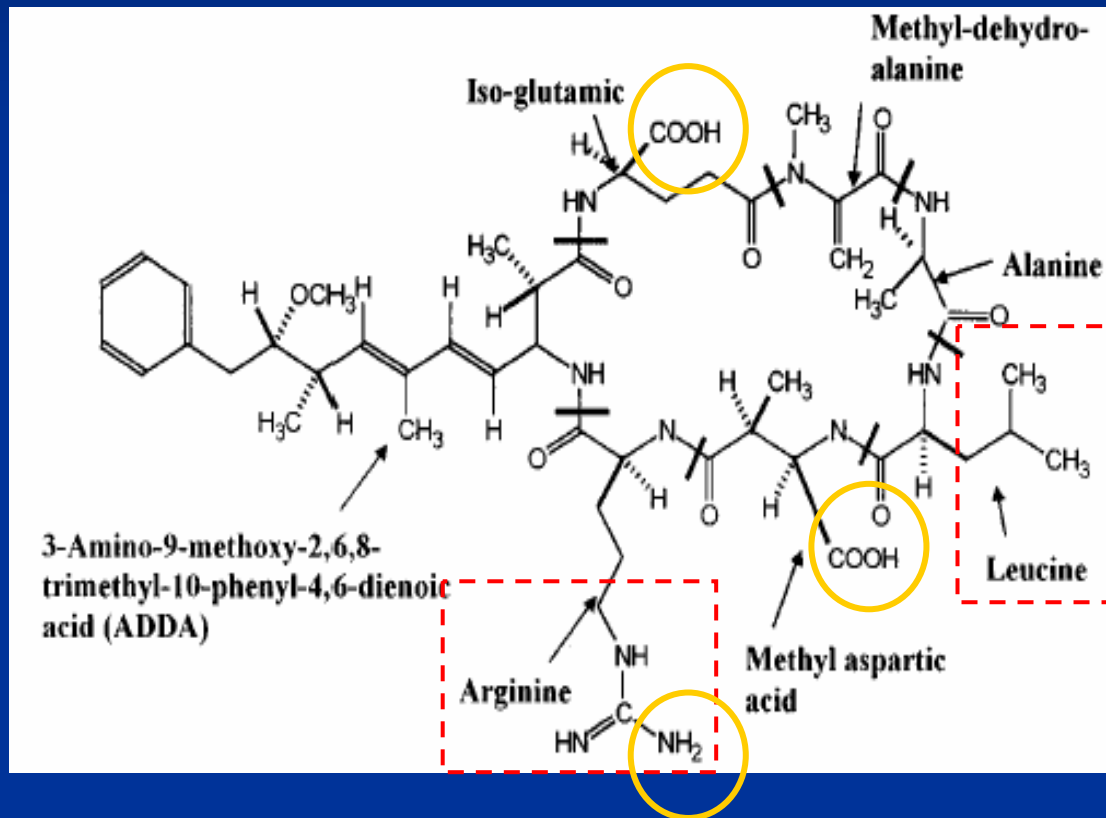
Removal of Microcystin-LR by UF membranes and Activated Carbon

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Characteristics of Microcystin-LR



- Cyclic heptapeptide structure
- Molecular weight: 995.18 (1000 Da)
- Size: 1.2-2.6 nm (Donati et al., 1994)
- pH_{PZC} : 2.09~2.19 (P. Gert-Jan De Maagd et al., 1999)
- Amphiphatic molecules containing hydrophilic functional groups and hydrophobic parts (Vesterkvist et al., 2003)

Effects of Microcystins on Humans

■ Exposure

- Microcystins - The most frequently occurring cyanobacterial toxin released from *microcystis* (Lawton and Roberson, 1999)
- Major routes - Recreational skin contact or consumption of contaminated waters (Codd et al., 1997)

■ Health Effects

- Inhibition of protein phosphatases 1, 2A (MacKintosh et al., 1990)
- Liver damage, Liver cancer tumor promoter (Carmichael, 1994)
- Affect the kidney and lungs (Hooser et al., 1990)
- Death - LD₅₀: 50 µg/kg of body weight in mice (Dawson, 1998)

■ Standards

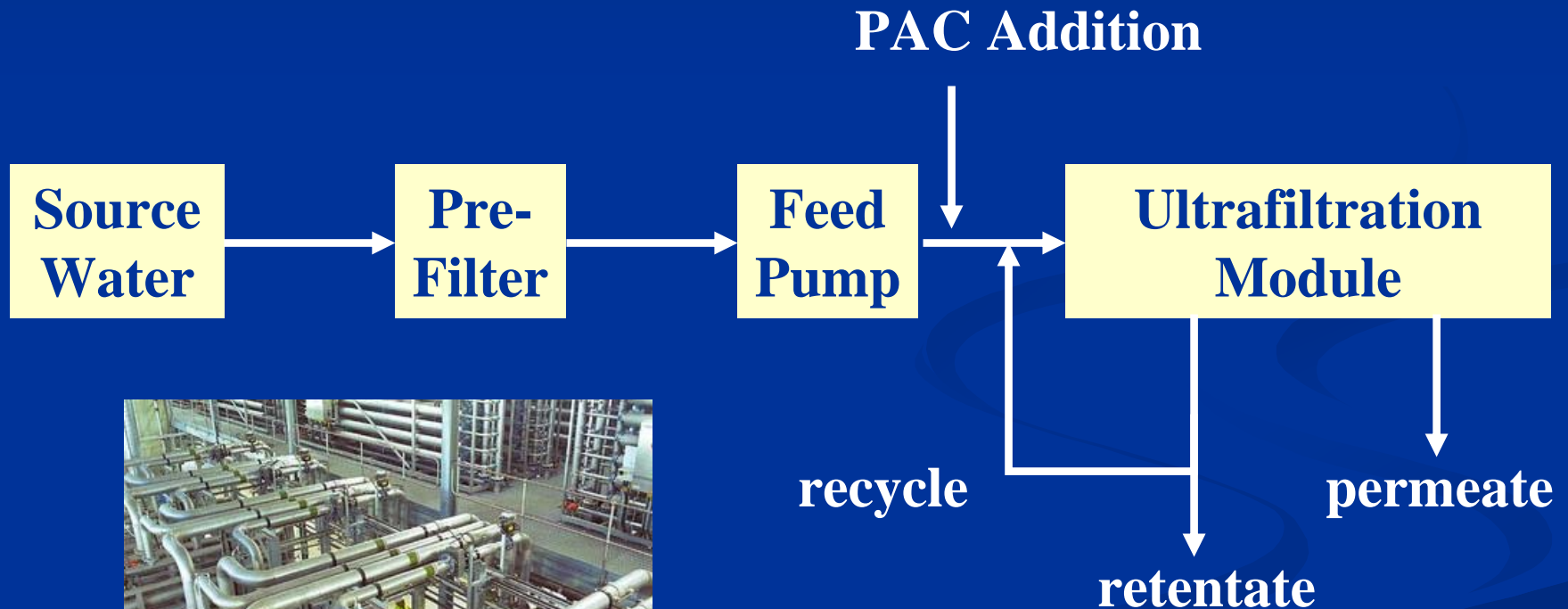
- USEPA candidate contaminant list
- WHO: Provisional guideline value for microcystin-LR of 1 µg/L

Treatment Processes for Removal of Microcystins

Processes	Advantages	Problems
Coagulation/ Flucculation ¹	Effective for particulate cell	Ineffective in removing dissolved toxins Possible cell lysis during treatment
PAC/GAC ⁴	Effective (>80%)	High PAC doses needed for WHO guideline DOC competition will reduce capacity and hasten breakthrough by saturated GAC filter
Chlorination ^{1,2}	Effective (>80%)	Disinfection by-products, High dose needed Inducing cell lysis and release of toxins
Ozonation ³	Very effective (>98%), Fast	Insufficient during blooms or high DOM conc. By-product due to incomplete oxidation
Membranes ¹	>99% rejection of NF or RO	UF/MF - Ineffective for dissolved toxins NF/RO - fouling problems due to NOM

1: Drikas et al., 2001, 2:Antoniou et al., 2005, 3:Hoeger et al., 2001 and Rositano et al., 2001,
4: Hart and Stott, 1993

PAC-Ultrafiltration Process Configuration



Advantages of PAC-UF System

PAC-UF System: The combination of PAC adsorption and UF membrane separation

- Ultrafiltration being utilized during design of **plant upgrades and new plants**
- PAC-UF emerging technology for the treatment of **organic micropollutants** in drinking water
- Effective for removing not only **turbidity** and **bacteria** cell but also **dissolved organic compounds**¹
- **PAC dosage is lower** compared with PAC adsorption process²
- **NOM fouling reduced**²

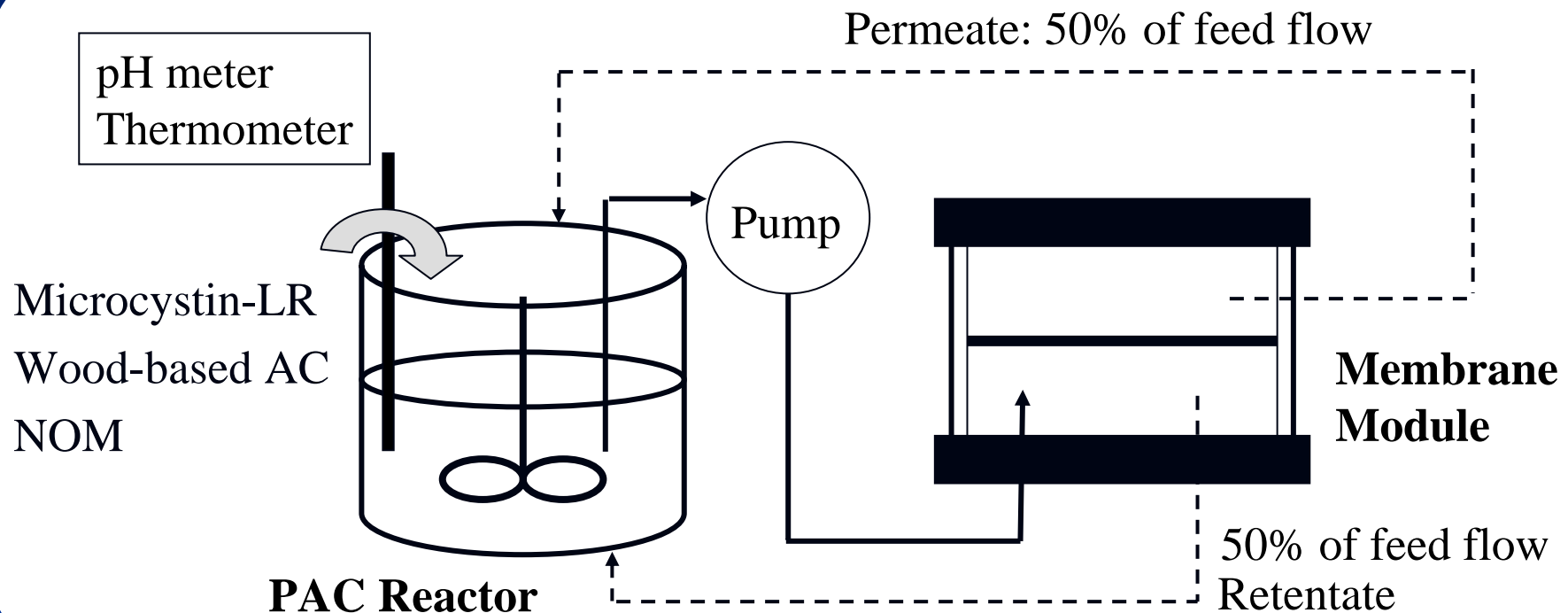
Study Objectives

- 1. Investigate the application of ultrafiltration coupled with PAC adsorption to remove microcystin-LR from drinking water**
- 2. Examine the effect of natural organic matter (NOM) on the removal of microcystin-LR by PAC adsorption, UF, and PAC-UF system**

Ultrafiltration coupled to PAC to remove microcystin-LR from drinking water

- 1. The effect of membrane characteristics**
- 2. The effect of PAC dosage**

Schematic of lab-scale PAC-UF system



Operating conditions

- pH: 7.0 ± 0.2 ; Ionic strength: 5mM NaHCO_3 ; Temp.: $22^\circ\text{C} \sim 24^\circ\text{C}$
- Operating pressure: 30 ± 10 psi for 20KDa, 55 ± 5 psi for 5KDa
- Initial feed flow: 1.2×10^{-3} L/sec, Initial permeate flux: 3.89×10^{-5} $\text{m}^3/\text{m}^2\text{-sec}$

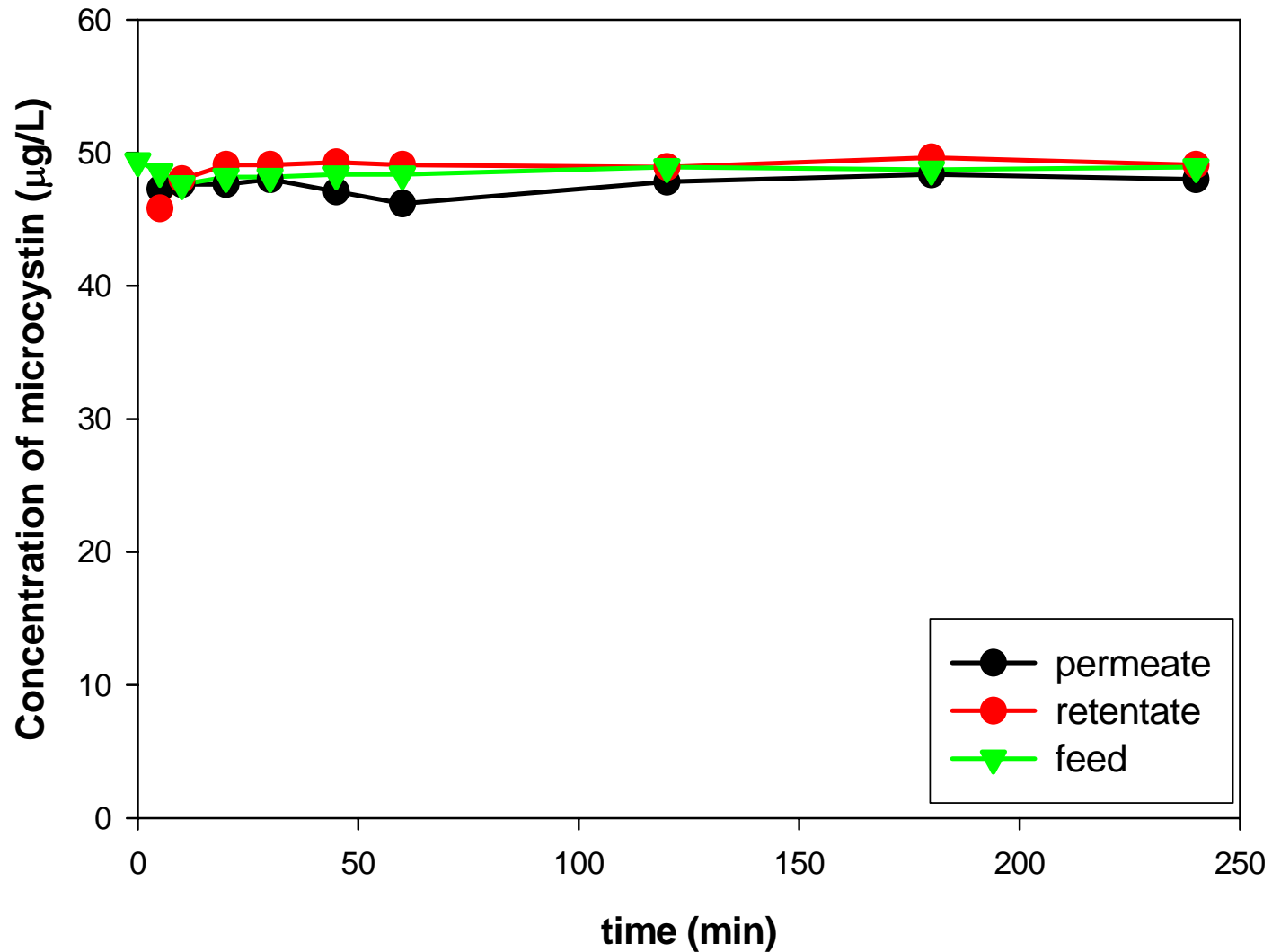
Characteristics of UF membranes

Membrane characteristics	CA 20KDa	PES 20KDa	PES 5KDa
Membrane surface material	Cellulose Acetate	Polyether-sulfone	Polyether-sulfone
MWCO ¹	20KDa	20KDa	5KDa
Contact angle ²	17.0	49.5	49.5
Zeta potential at pH 7	-9.31	-13.16	-12.99

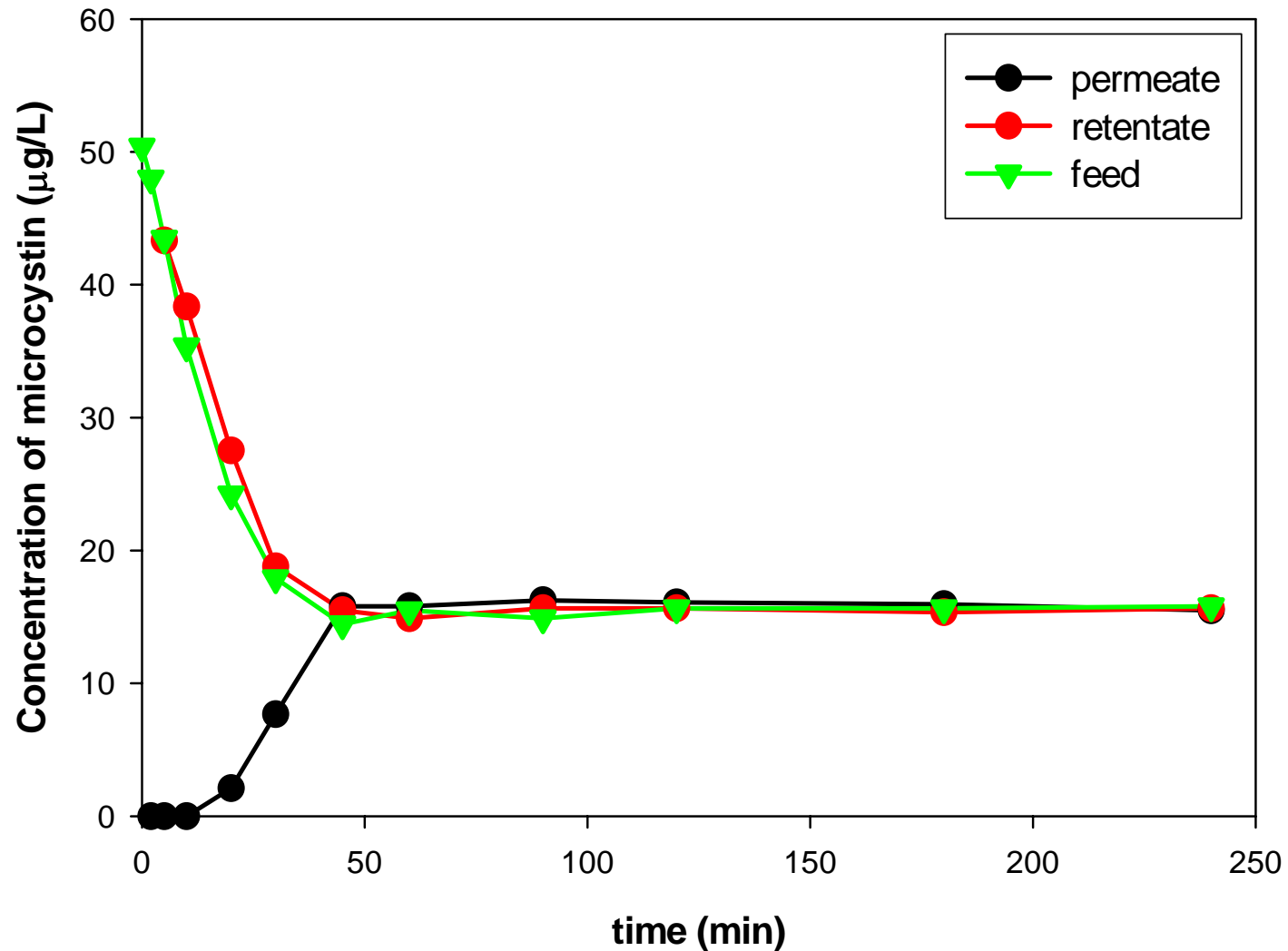
1. Manufacturer's values (GE Osmonics)

2. Cho et. al, Desalination, 1998

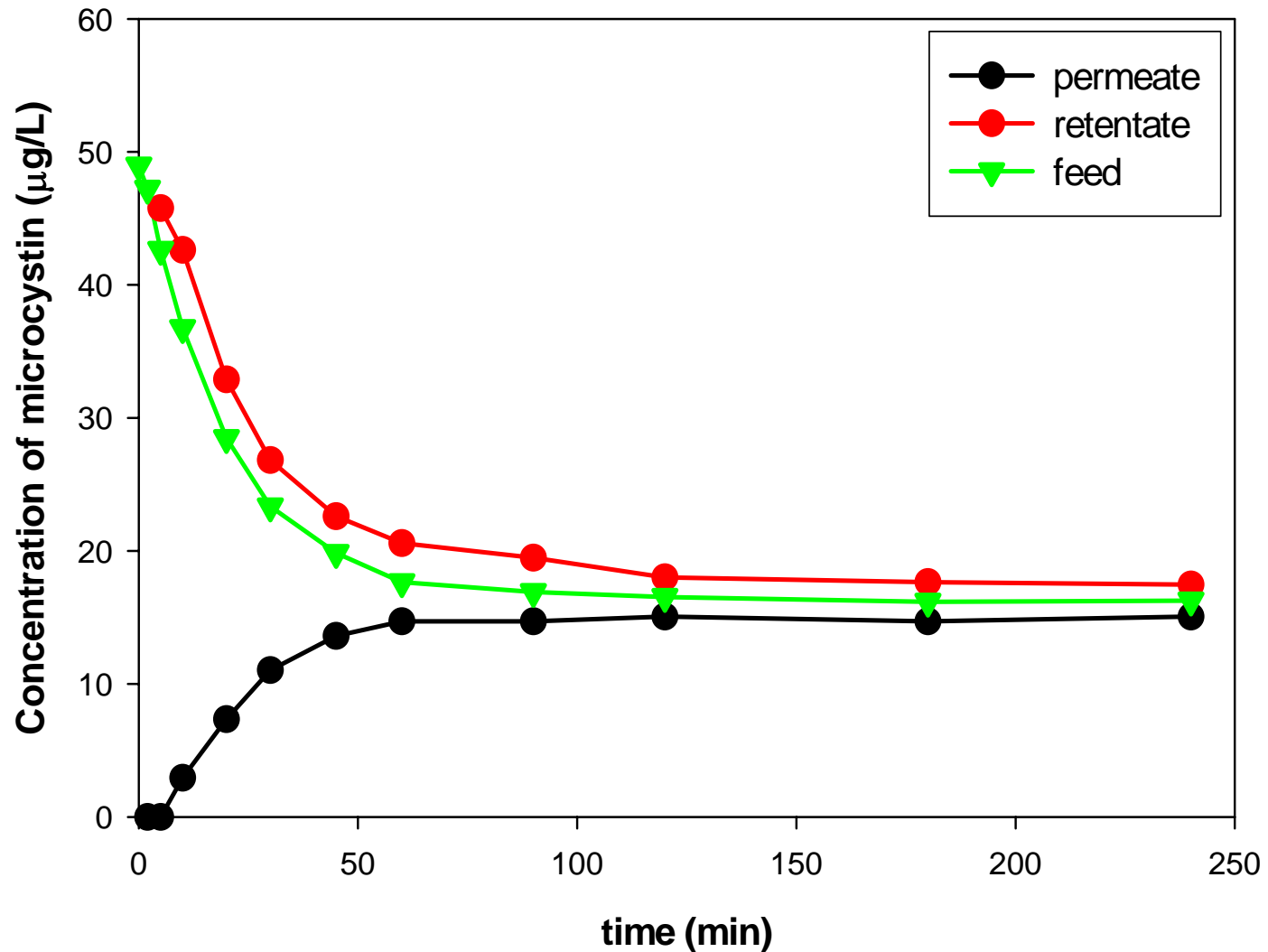
Ultrafiltration: CA-20KDa



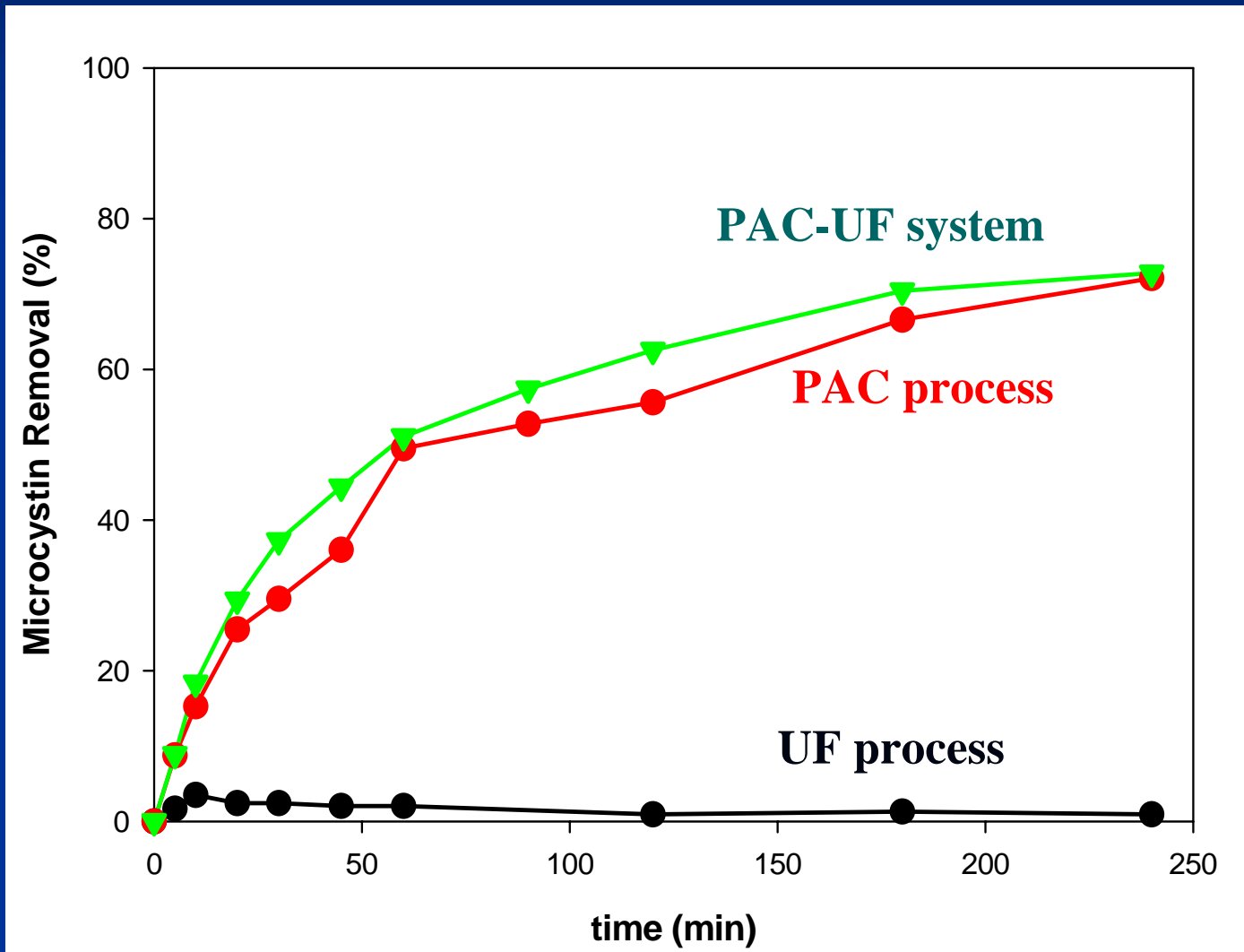
Ultrafiltration: PES-20KDa



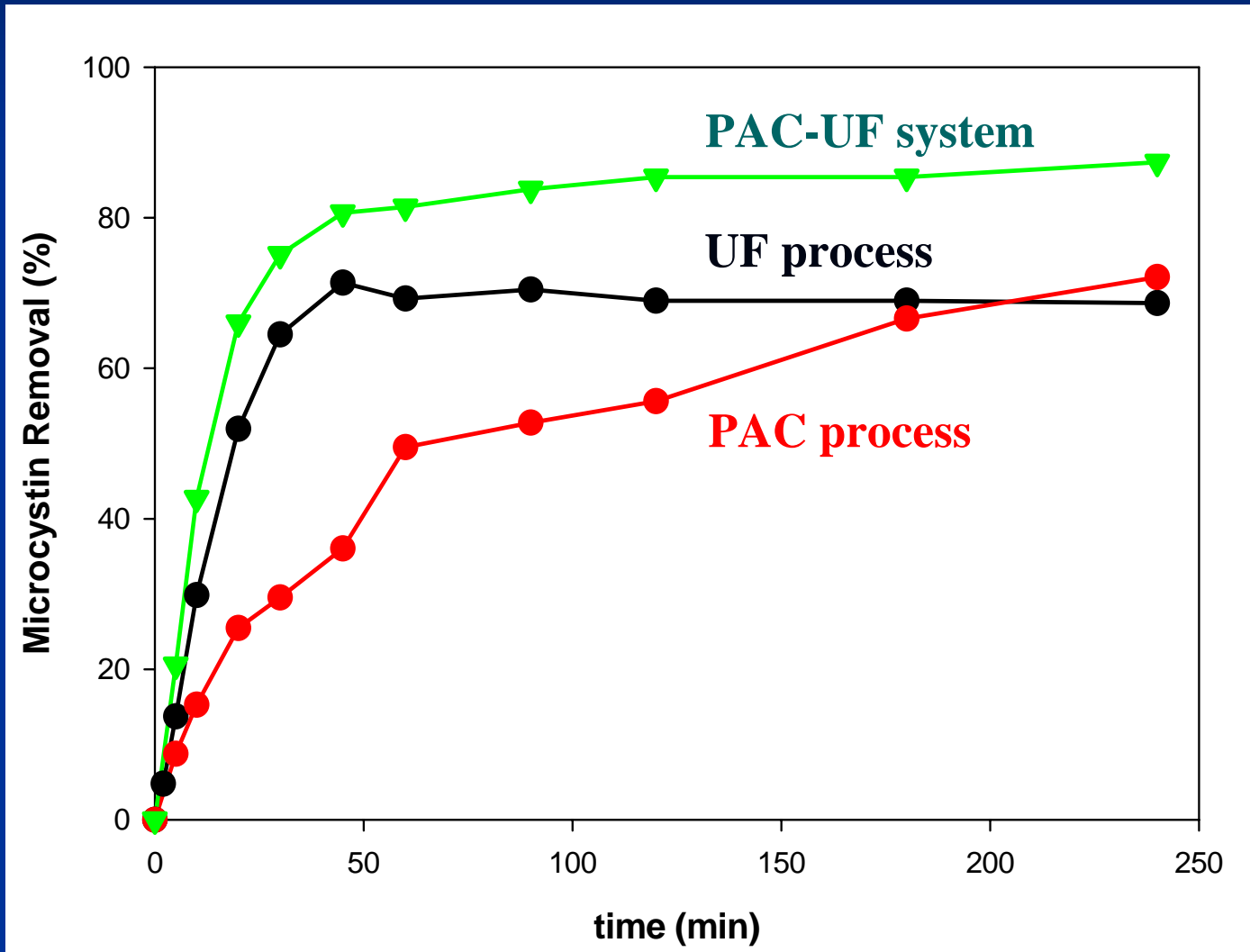
Ultrafiltration: PES-5KDa



PAC-UF: 2ppm wood-based carbon and CA-20KDa membranes

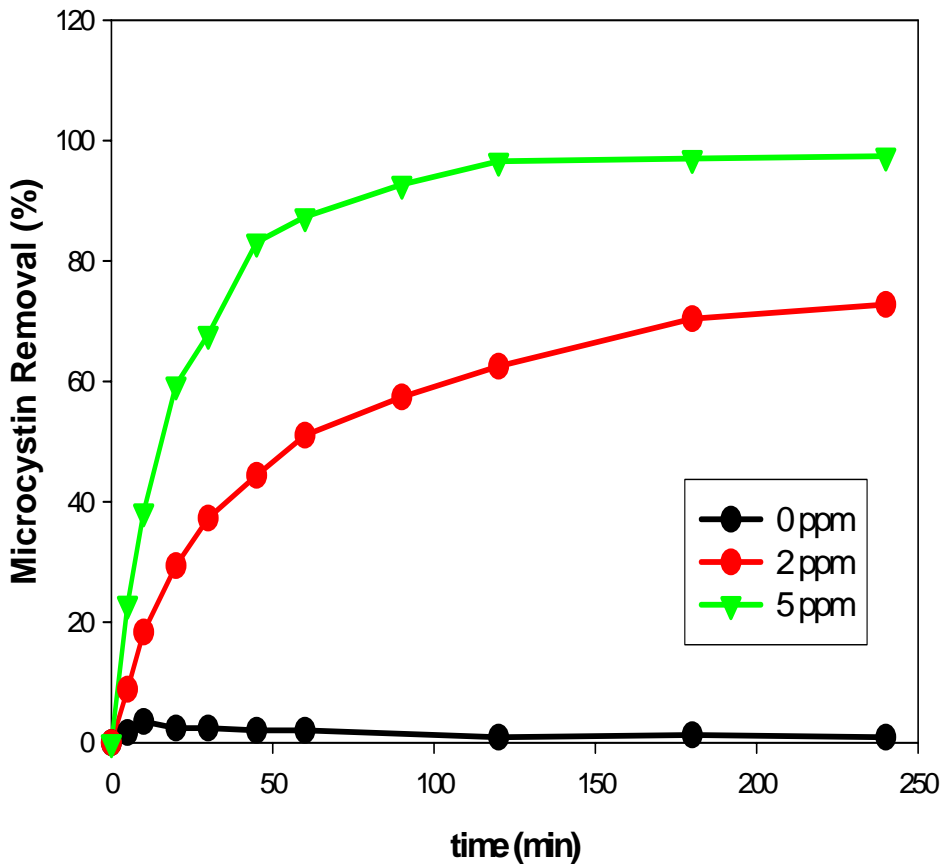


PAC-UF: 2ppm wood-based carbon and PES-20KDa membranes

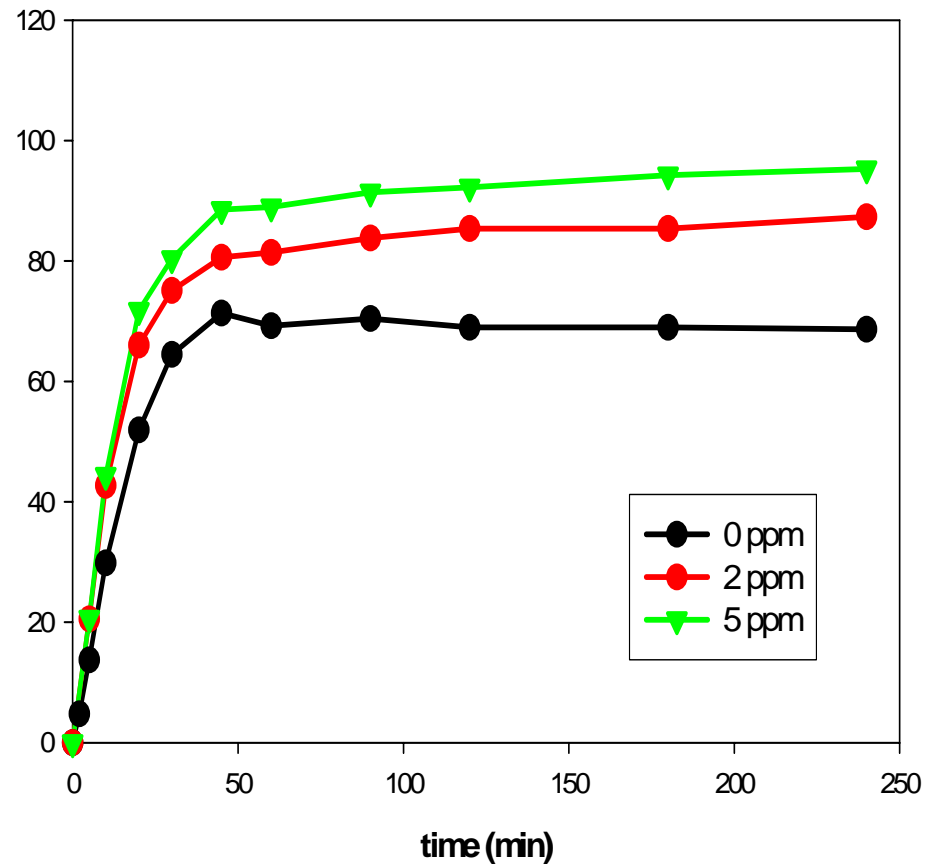


The effect of PAC dosage

CA-20KDa



PES-20KDa



Effect of SRFA on the removal of microcystin-LR

- 1. The effect of SRFA on membrane fouling during UF**
- 2. The effect of SRFA on the removal of microcystin-LR by a PAC-UF system**

Effect of SRFA during UF

Simultaneous Addition

MC-LR + HS

**Clean-UF
membranes**

Sequential Addition

HS

**Clean-UF
membranes**

MC-LR

**Fouled-UF
membranes**

Characteristics of Aquatic Humic Substances

Characteristics	Suwannee River Fulvic Acid
Molecular weight	1000-1500 Da ¹ 2324 Da ²
Acidic functional groups ³	Carboxyl group: 11.44 meq/g C Phenolic group: 2.91 meq/g C
¹³ C NMR Estimates of Carbon Distribution ³	Aromatic: 24% Aliphatic: 33%

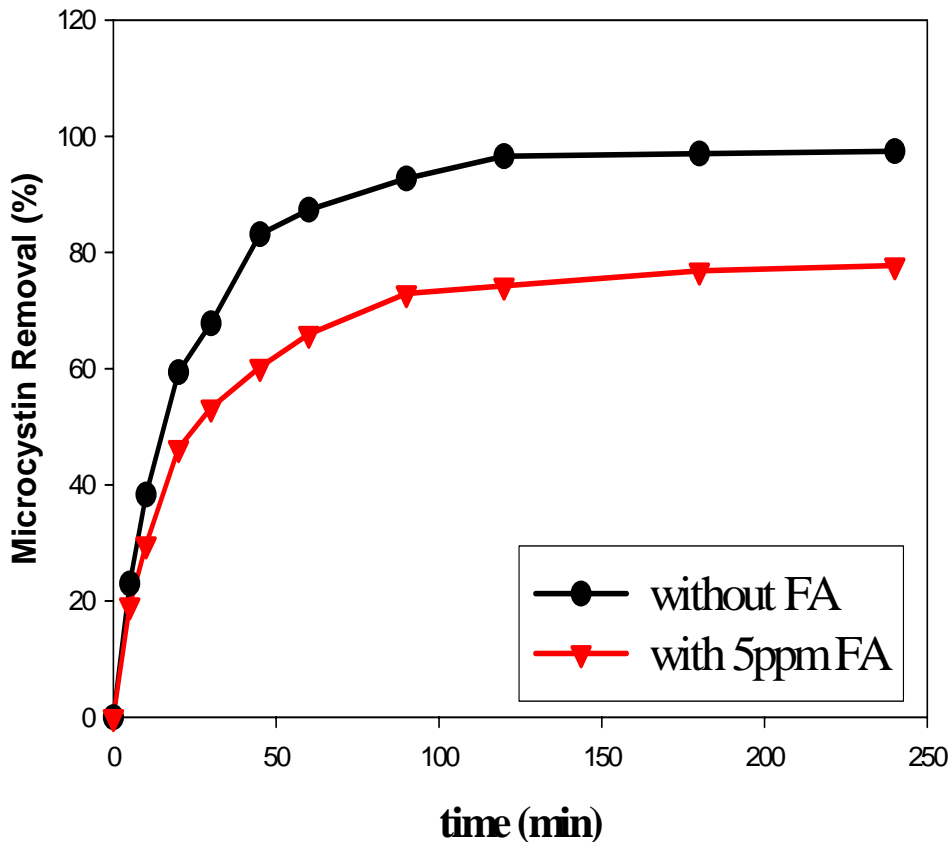
1. Thruman, 1982 – using small-angle X-ray scattering
2. Chin et al., 1994 – using HPSEC technique
3. IHSS website

Changes in permeate flux and pore sizes

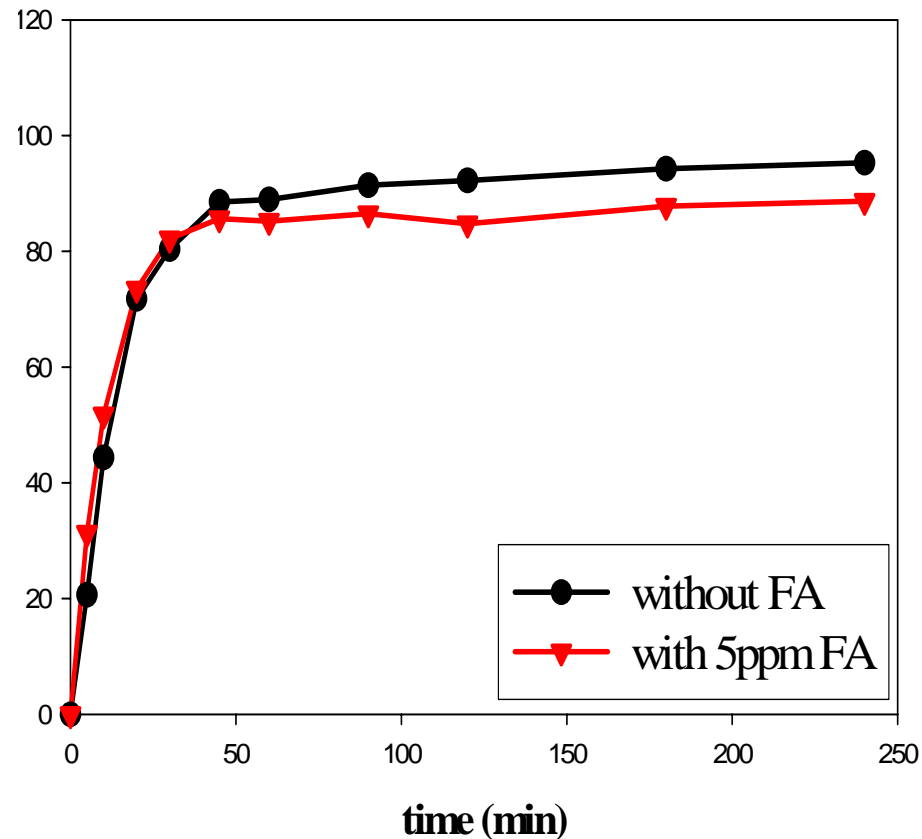
Membranes		Permeate flux (m ³ /m ² -sec)	PEG rejection for 1000 Da (%)
CA-20KDa	Clean	3.87×10^{-5}	-
	FA-fouled	3.87×10^{-5}	-
PES-20KDa	Clean	3.87×10^{-5}	0.4
	FA-fouled	3.35×10^{-5}	3.6
PES-5KDa	Clean	3.87×10^{-5}	7.7
	FA-fouled	3.23×10^{-5}	9.8

Effect of SRFA on microcystin-LR removal by PAC-UF

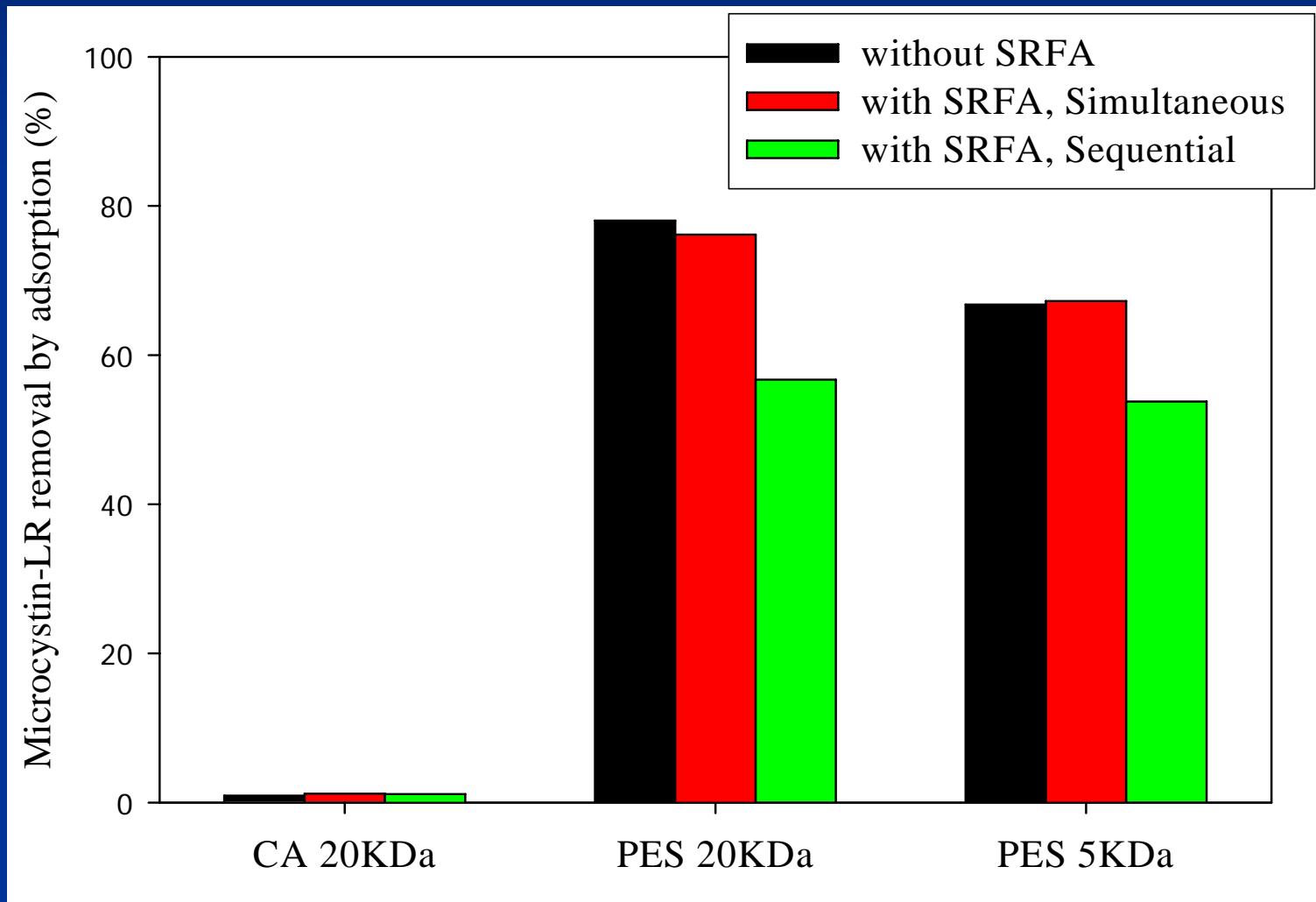
CA-20KDa



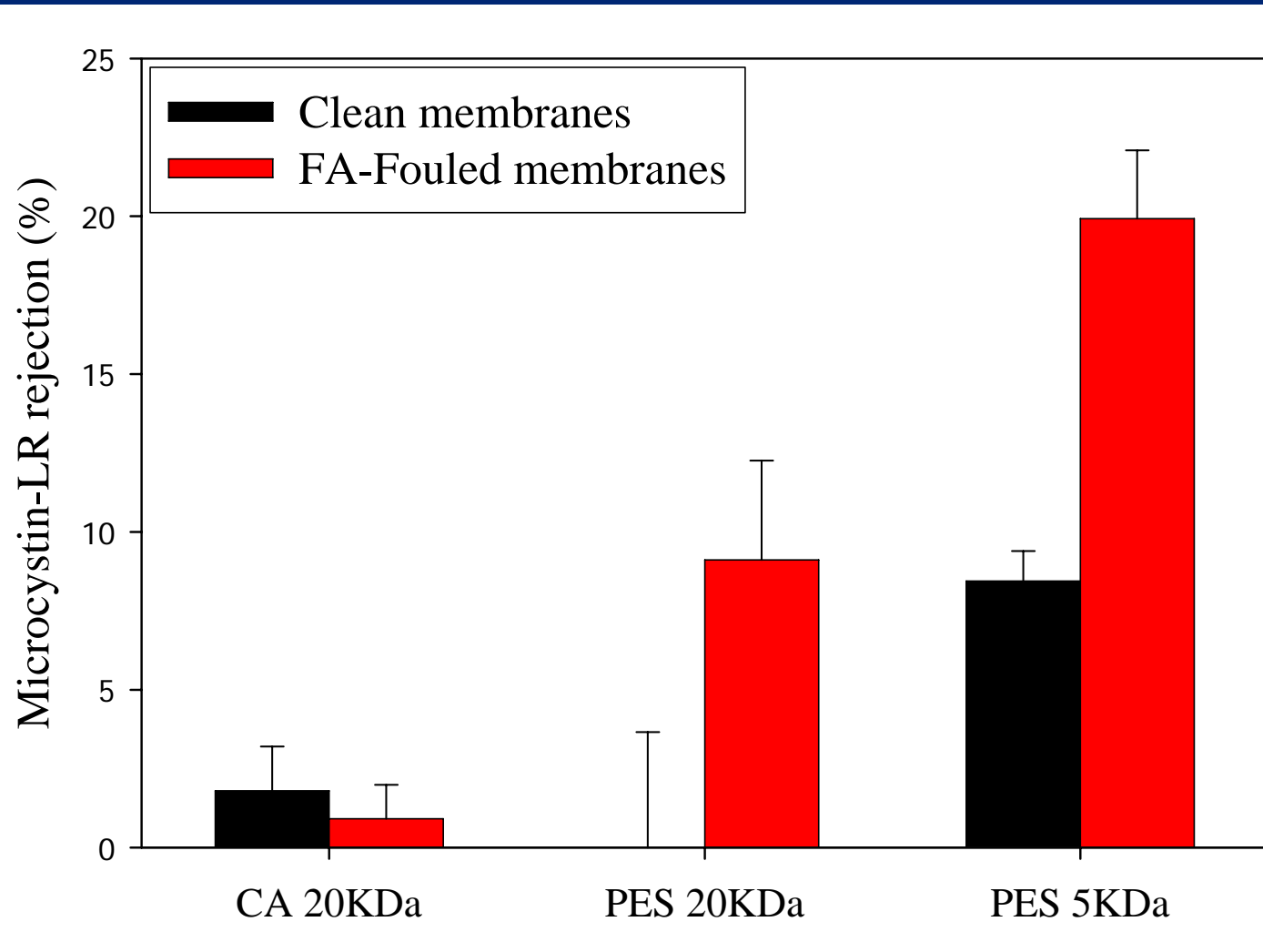
PES-20KDa



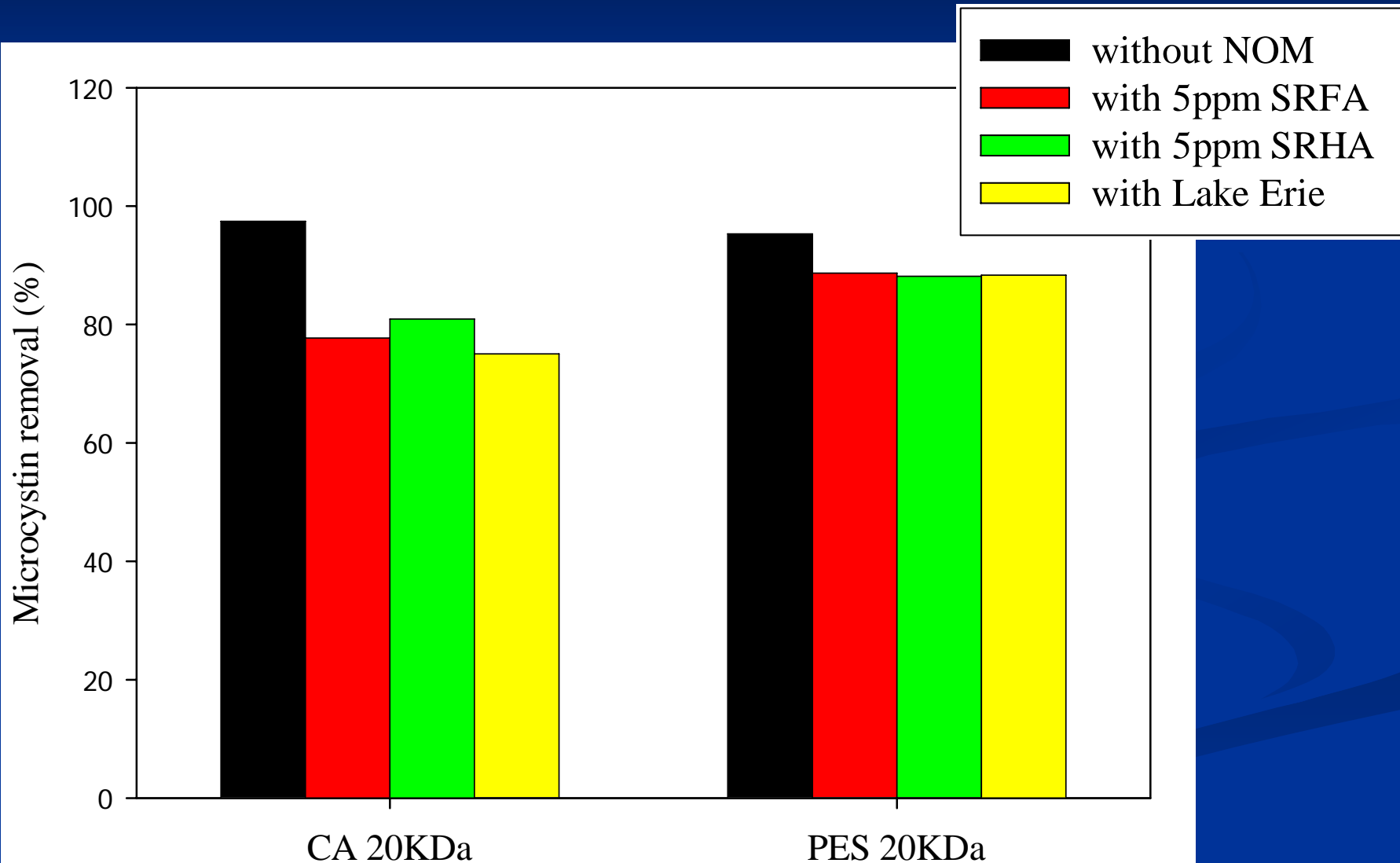
SRFA reduces membrane adsorption capacity for microcystin



Rejection of microcystin increases when hydrophobic membranes fouled by NOM



Type of NOM has little effect on removal (PAC-UF; 5ppm PAC)



Conclusions

- UF-PAC effectively removes microcystin-LR from drinking water.
- Membrane pore size and composition influence removal
 - Hydrophobic membranes adsorb microcystin
 - Smaller pore size results in greater rejection
- Presence of natural organic matter hinders microcystin removal by PAC-UF, due primarily to competition for sorption sites on PAC

Acknowledgments

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